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The Synthesis of Hybrid Materials by the Blending of Polyhedral Oligosilsesquioxanes into Organic Polymers

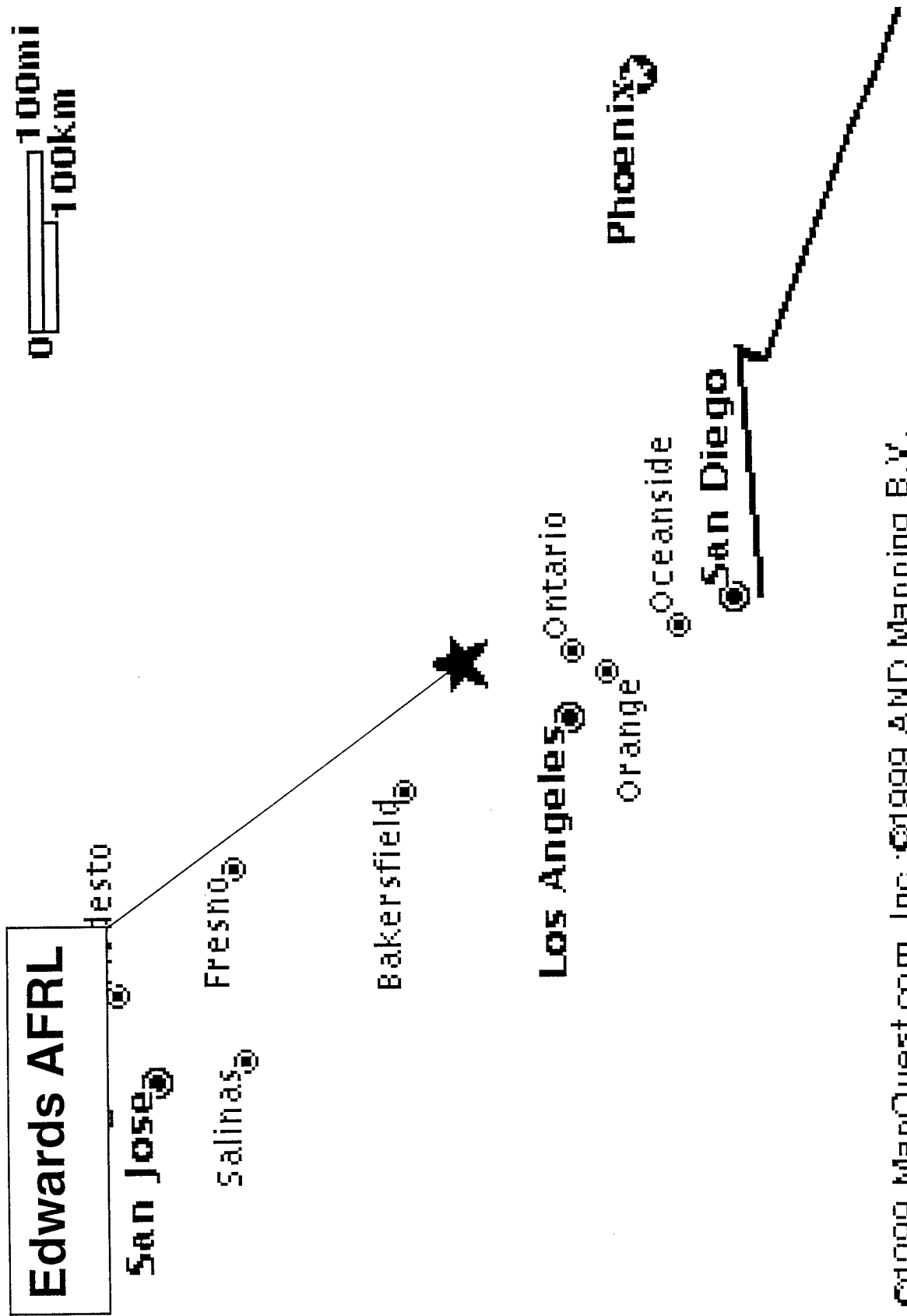
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Hybrid Organic/Inorganic Blends

- GOAL: To study the interaction and solubility of Polyhedral Oligosilsesquioxane (POSS) molecules containing various organic side groups with the polymer matrix
- Polystyrene was chosen since it is readily available and can easily be solvent cast with the POSS molecules for TEM studies

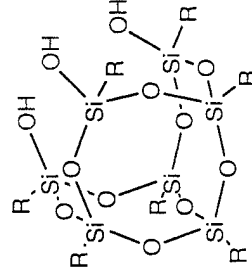


Why Use Blendables?

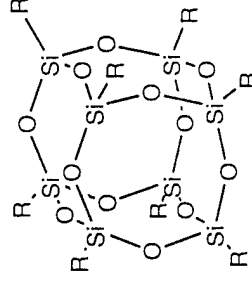
- Easier to tailor the organic side groups of the POSS molecule to give a polymer-soluble species
- Simple blending techniques can be used instead of copolymerization with reactive POSS monomers
- Potential Drop-in molecular modifier without requiring expensive replacement of processing equipment

POSS = Polyhedral Oligomeric Silsesquioxane

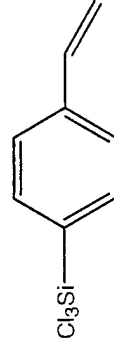
General Synthesis



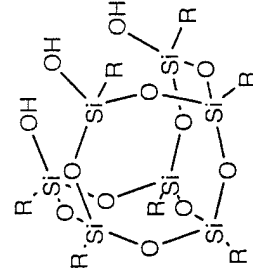
R = cyclopentyl
vinyl



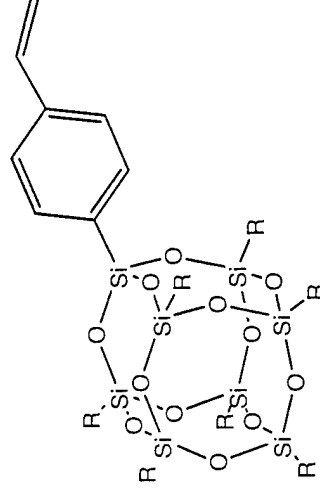
R = cyclopentyl
vinyl



THF, NEt_3 - $\text{NEt}_3 \cdot \text{HCl}$



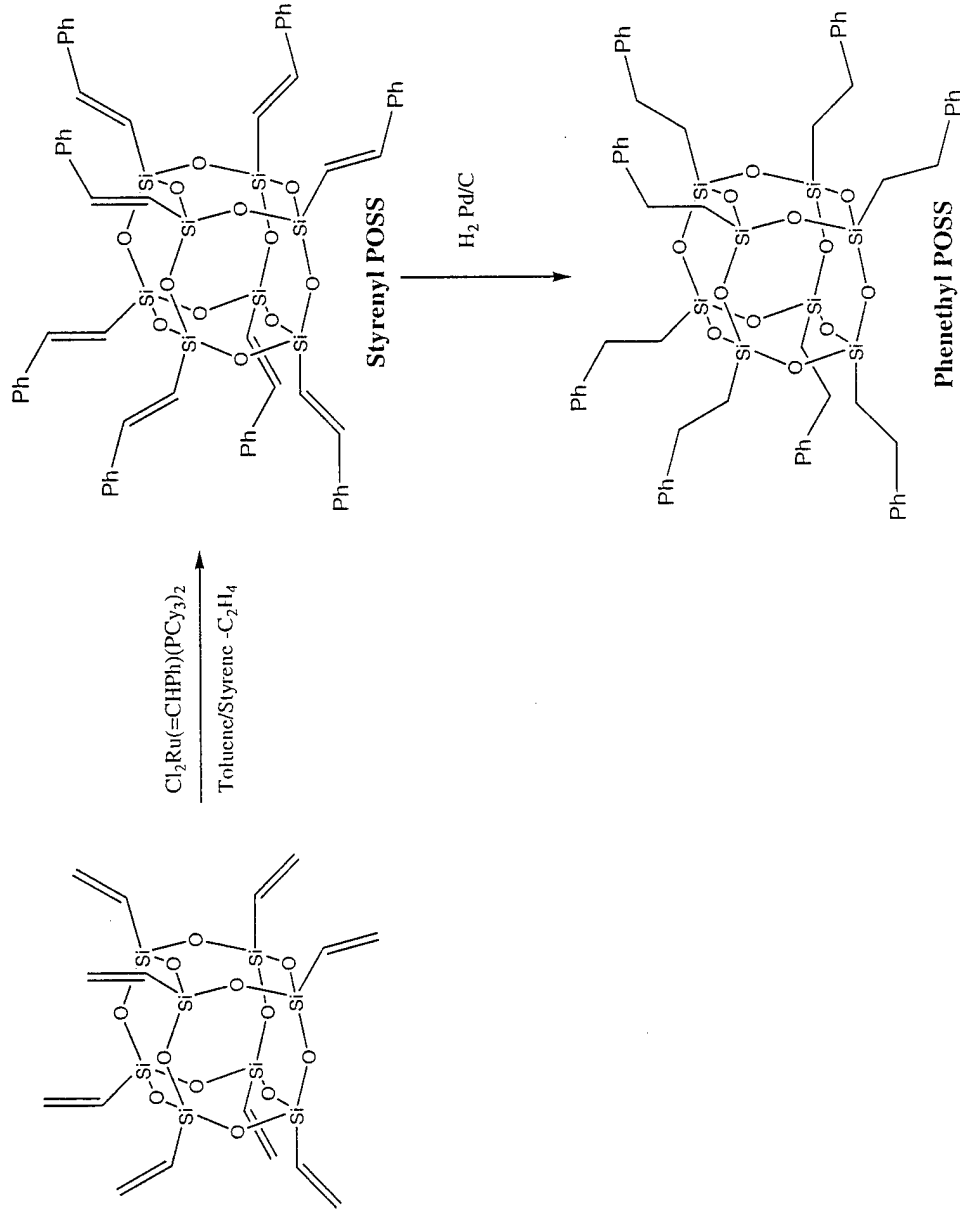
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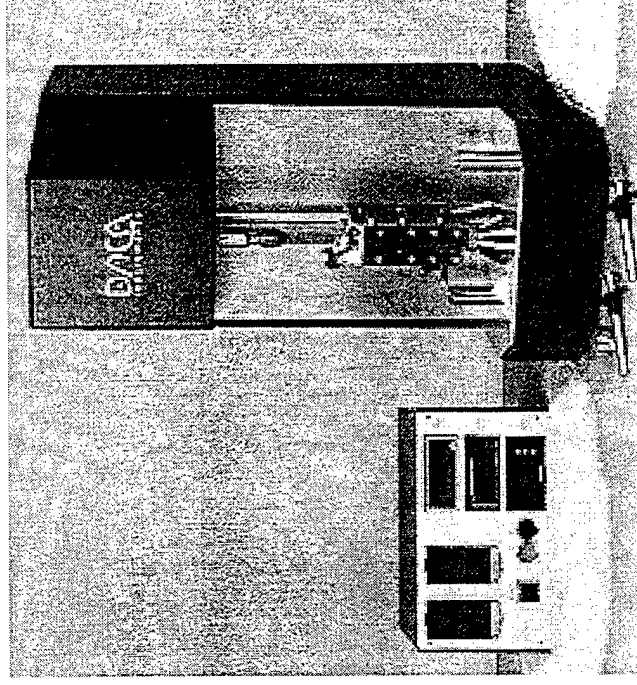
POSS = Polyhedral Oligomeric Silsesquioxane

General Synthesis



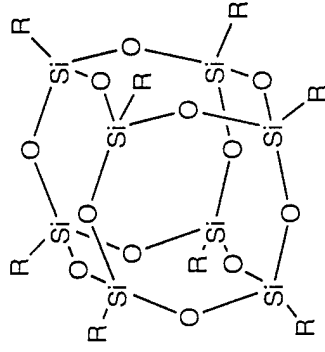
Preparation of Styrene-POSS Blends

- TEM Method
- Dissolve the Styrene and POSS in THF
- Cast very thin film by slow solvent evaporation
- Traditional Processing
- Place Polystyrene in Extruder
- Add POSS
- Blend 2-5 Minutes



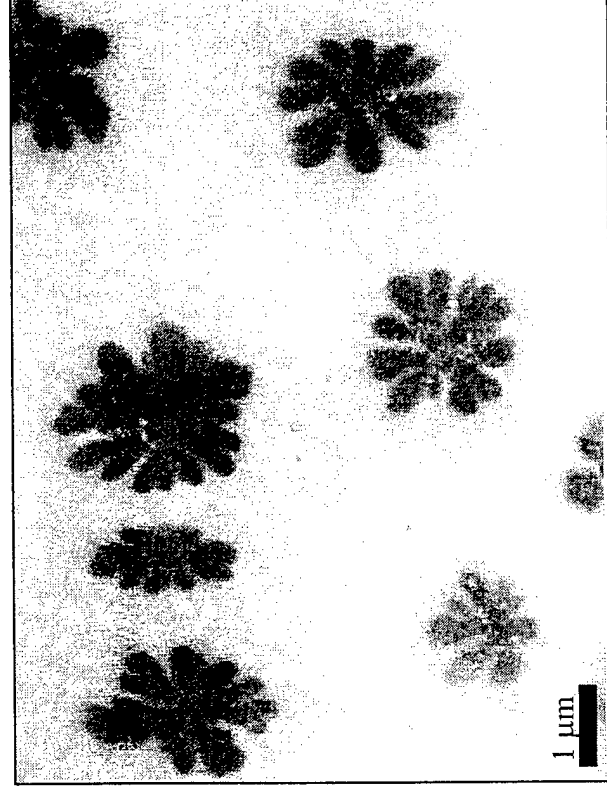
POSS Blends - Crystal Formation

50 wt % Cp_8T_8 in 2 million mol. wt. Polystyrene



R = cyclopentyl

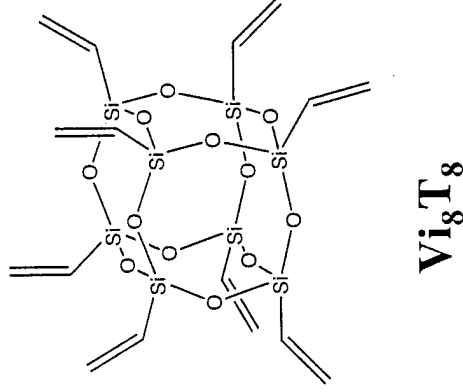
Cp_8T_8



TEM image clearly shows formation of immiscible POSS crystallites (20-50k molecules)

POSS Blends - Crystal Formation

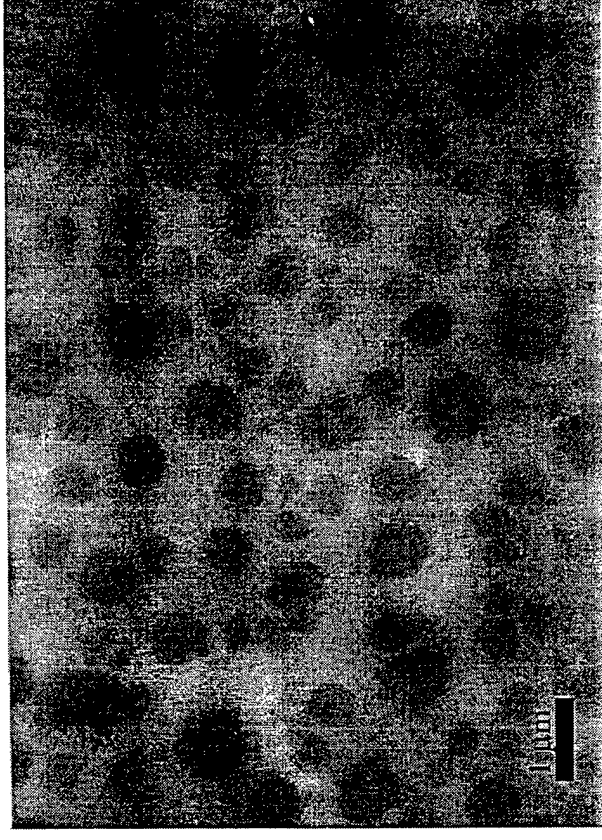
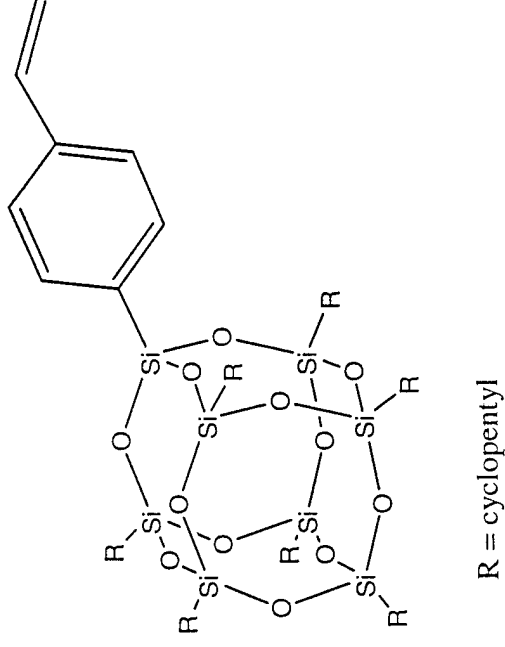
50 wt % Vi_8T_8 in 2 million mol. wt. Polystyrene



TEM image clearly shows immiscibility in polymer system

POSS Blends - Increased Solubility

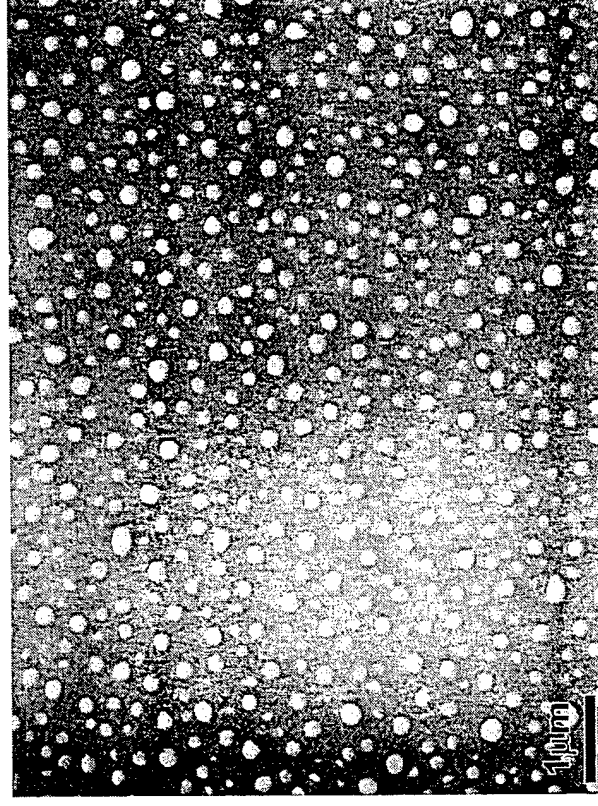
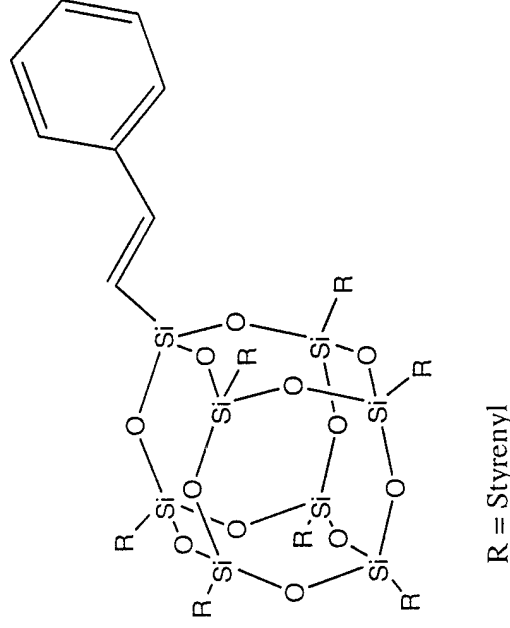
50 wt % Cp₇T₈Styryl in 2 million mol. wt. Polystyrene



TEM image shows significant decrease in size of crystallites

POSS Blends - Miscibility

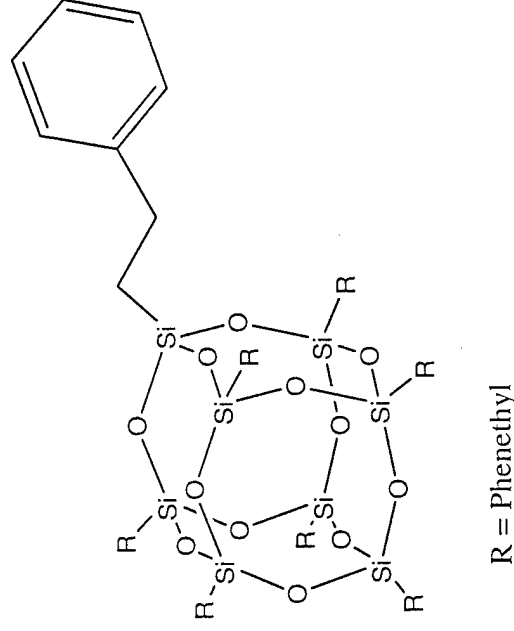
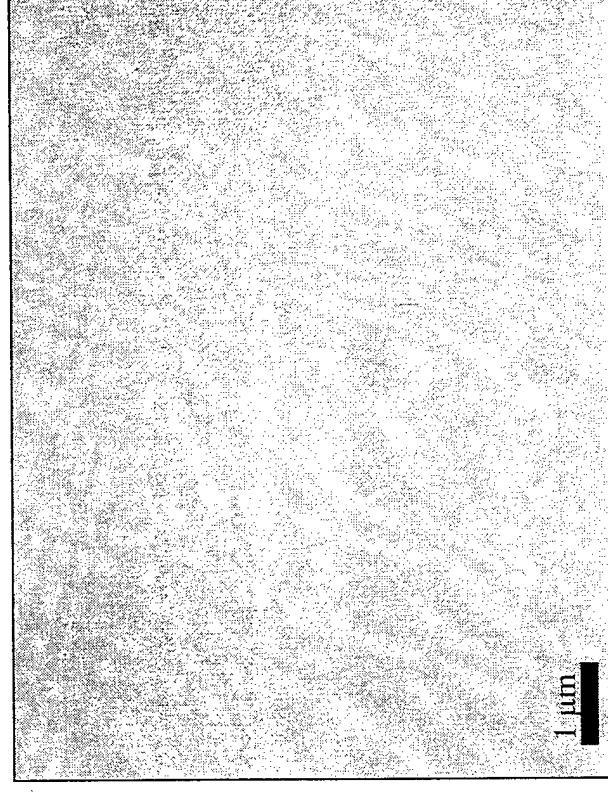
50 wt % Styrenyl₈T₈ in 2 million mol. wt. Polystyrene



- White domains represent pure polystyrene (process issue)
- Grey domains represent miscible POSS/polystyrene
- Black dots are POSS crystallites (<100 POSS molecules)
- 30% increase in surface hardness of the material

POSS Blends - Miscibility

50 wt % Phenethyl₈T₈ in 2 million mol. wt. Polystyrene



- **Demonstrated Complete Miscibility!!**
- **Grey domains represent miscible POSS/polystyrene**
- **Black dots are POSS crystallites (<100 POSS molecules)**



Conclusions

- The organic side groups on the POSS molecule are extremely important in determining the solubility of the POSS in polystyrene
- The addition of the more soluble styrenyl POSS into styrene leads to an increase in surface hardness without adversely affecting polymer properties
- POSS can be thought of as functionalized silicas with the side groups acting as solubility enhancers



Acknowledgements

- AFRL Propulsion Directorate
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